ICE VII, THE DENSEST FORM OF ICE*

By Barclay Kamb and Briant L. Davis

CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, AND
SOUTH DAKOTA SCHOOL OF MINES AND TECHNOLOGY, RAPID CITY

In the pressure range 0–25 kilobars there occur 7 different crystalline modifications of ice,[1] whereas from 25 kbar up to the highest pressure so far tried, 200 kbar, only a single form occurs:[2] ice VII, of density about 1.7 gm cm^{-3}. Ice VII thus seems in some sense to be an "ultimate" crystalline form of ice, and its structure is therefore of considerable interest, particularly in relation to the structures of the lower-pressure forms, for which some information is already available.[3, 4]

The question of the "ultimate" high-pressure structure of ice can be treated hypothetically by considering that in the high-pressure limit a closest packing of the oxygen atoms of the water molecules should be approached. At the same time maximum stability should correspond to a strong network of hydrogen bonds in the crystal, and the conditions for this[4] are not completely compatible with closest packing of the oxygen atoms. In hexagonal closest packing[5] there would be available coordination angles O—O—O of 109.5°, favorable as donor angles for hydrogen-bonded water molecules thus: O . . . H—O—H . . . O; and there are also angles of 90°, somewhat less favorable. However, none of these coordination angles lie in mutually perpendicular or nearly perpendicular planes, so that favorable conditions at the acceptor end of the hydrogen bonds[4] cannot hold. In cubic closest packing possible donor and acceptor angles in mutually perpendicular planes would exist, and a network of hydrogen bonds through the structure could be constructed, as shown in Figure 1. However, the donor angles would be 90°, whereas angles closer to 104.5° the H—O—H angle of the free water molecule,[6] would be more favorable.

Improved donor angles can be achieved by a distortion of the structure of Figure 1, in which the a_3 axis contracts by a factor $\sqrt{2/3}$ while the a_1 and a_2 axes lengthen by a factor $2/\sqrt{3}$. The resulting structure (Fig. 2) has a body-centered-cubic arrangement of the oxygen atoms. The distortion from structure 1 to structure 2 is achieved at the expense of an increase in volume by the factor $4\sqrt{2}/3\sqrt{3}$, a 9 per cent increase over closest packing (for fixed hydrogen bond length). This destabilizing feature, for a high-pressure phase, is offset by the increase in donor angle from 90° to 109.5°, and by removal of 4 of the 8 nonhydrogen-bonded nearest neighbors in structure 1 to a distance 16 per cent greater in structure 2, which should result in a large decrease in the repulsive energy. Moreover, an important entropy stabilization can be achieved because in structure 2 the protons can be disordered[7] as they are in ice I, whereas in structure 1 the protons would have to be ordered (as shown in Fig. 1), unless the unfavorable donor angles of 120° were to be used.

Because the hypothetical structure in Figure 2 is a simple one, differing in this respect from the relatively more complex structures known for other high-pressure forms of ice,[4] we undertook to test it by obtaining X-ray powder diffraction data for ice VII by high-pressure X-ray techniques.

Experimental Method.—The apparatus used for obtaining X-ray diffraction data of samples at high pressure has been described by David and Adams.[8] The sample is contained in a hollow beryllium cylinder, and is compressed between a tungsten
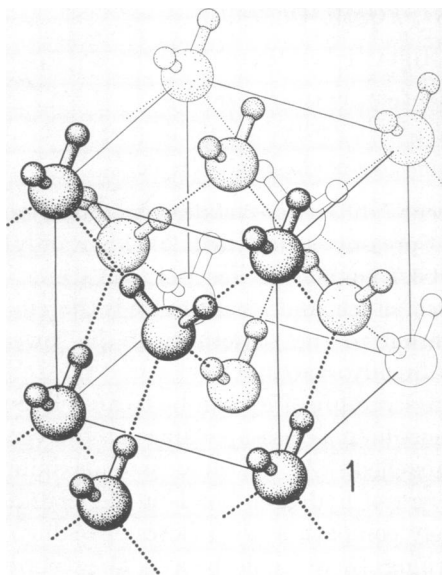
FIG. 1.—Hypothetical cubic-closest-packed structure for high-pressure ice. The water molecules are shown in a conventional representation, and the hydrogen bonds are indicated by dotted lines.
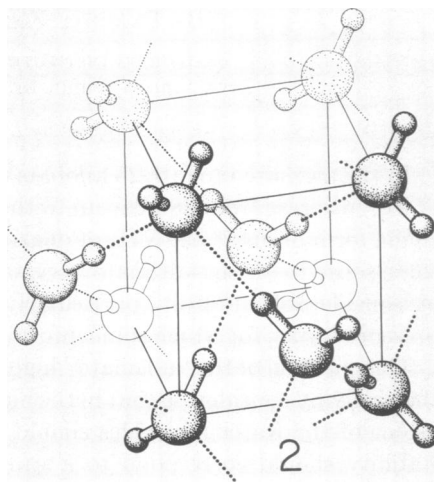
FIG. 2.—Body-centered structure obtained from structure 1 by contraction in the vertical (a_3) direction and extension in the horizontal (a_1, a_2) directions. The a_1, a_2 cubic axes of the body-centered cell lie at 45° to those of structure 1. The protons in structure 2 are shown disordered. This is the structure of ice VII.

carbide piston and a 1-mm-thick beryllium disk supported in turn by a second tungsten carbide piston. With pistons of diameter 3.2 mm or 2.6 mm, nominal pressures of more than 30 kbar can be reached in our apparatus. Piston friction reduces the actual sample pressure below the nominal pressures quoted. We made no attempt to measure the friction correction in these experiments, but previous experience with the apparatus[8] indicates that at pressures of about 25 kbar the correction is not more than about 4 kbar. This is confirmed by the nominal pressure of 23 kbar found for partial transformation to ice VII, which exceeds the expected pressure[1, 9] by no more than 2 kbar.

The samples were prepared by crushing a small amount of ordinary ice and spreading the powder to a thickness of about 1 mm on the lower piston of the bomb (precooled). The temperature of the sample was controlled by passing a regulated stream of liquid nitrogen through a cylindrical jacket surrounding the bomb. A thermocouple was used to monitor the bomb temperature in a well at a point 9 mm distant from the actual sample.

No special precautions were made to seal the sample, other than the usual ones of having tight-fitting pistons and beryllium pellet. It was found that at pressures above the minimum melting pressure of water (2.0 kb), the seal breaks and the sample is expelled violently as soon as the temperature rises approximately to the minimum melting temperature of −22°C, regardless of the higher melting point at the actual sample pressure. This shows that pressures considerably lower than the nominal pressure are accessible to the sample as sealed, but lead to a leak only when
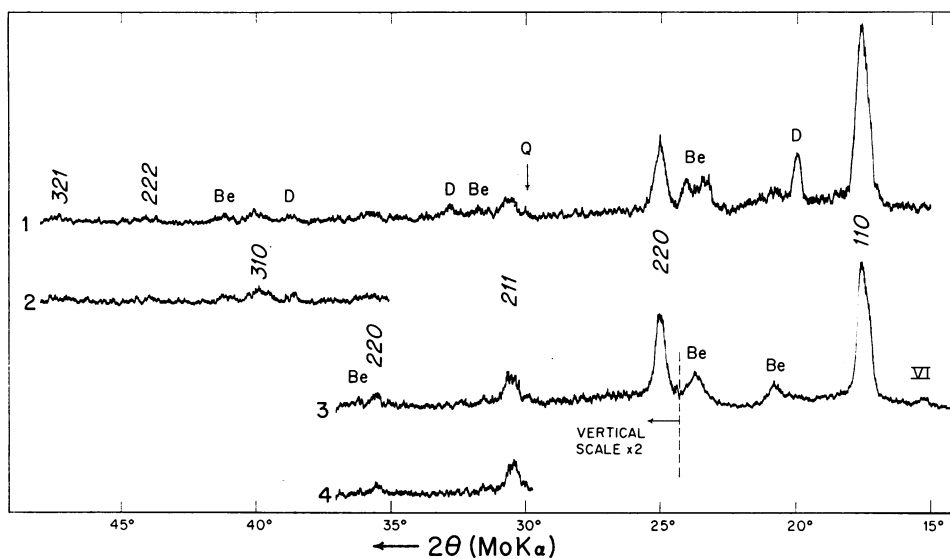
FIG. 3.—X-ray diffractometer tracings for ice VII under pressure, obtained with Mo Kα radiation. The ice VII peaks are indexed, peaks due to the beryllium of the high-pressure bomb are labeled *Be*, and those due to diamond (curves 1 and 2 only) are labeled *D*. Traces 1 and 2 were obtained at nominal pressure 30 kbar, using pistons of diameter 3.2 mm, traces 3 and 4 at 27 kbar (nominal), piston diameter 2.6 mm, all at −50°C. Actual sample pressure is about 25 kbar. In trace 3 the sample contained a small remnant of ice VI, as indicated by the peak labeled VI (the d = 2.71 A peak of ice VI, see Table 2).

a fluid phase forms. This situation probably obtains in all "squeezer"-type high-pressure experiments.

Results.—We have obtained powder patterns of ices II, V, VI, and VII within their fields of stability. The patterns of II and V could be recognized from powder data already at hand from quenching experiments.[4, 10] Ice VI appeared above the appropriate pressure of about 7 kbar, and VII above about 22 kbar. The reaction rates, as judged from the rate of change of the X-ray patterns, were strongly temperature-sensitive. Patterns for ice VII are given in Figure 3. Results for the other forms will be reported elsewhere.

Powder data for ice VII, determined from the patterns of Figure 3, are listed in Table 1. As an internal standard for measurement of the d-spacings, powdered diamond was included in some of the ice samples (Fig. 3). The diamond spacings were calculated from the spacings at atmospheric pressure by assuming a constant compressibility[11] of 0.18×10^{-6} bar^{-1}. The d-spacings for ice VII conform to a

TABLE 1

X-RAY DATA FOR ICE VII AT 25 KBAR, −50°C

d_{obs}	d_{calc}	hkl	I_{obs}	I_{calc}
2.34 A	2.33 A	110	100	100
1.64$_5$	1.65	200	32	26
1.35	1.35	211	9	10
1.16	1.17	220	4	4.5
1.04	1.04	310	6	3
0.95	0.95	222	2	2
0.88	0.87	321	1.5	1

Calculated values for a = 3.30 A, structure of Fig. 2.

body-centered cubic cell of edge $a = 3.30 \pm 0.01$ A. The two lines at shortest spacings are too weak to be well defined in the patterns, but are nevertheless recognizable.

If the unit cell contains two water molecules, the calculated density of ice VII at 25 kbar is 1.66 gm cm^{-3}. Bridgman did not report accurate measurements of the density, but stated[1] that "the specific volume is about 0.60 cm^3 gm^{-1} at 50,000 kg cm^{-2} pressure," corresponding to a density 1.67 gm cm^{-3}. This should be corrected to 1.56 gm cm^{-3} because of the expansion of 0.04 cm^3 gm^{-1} measured by Bridgman between 45 kbar and 20 kbar. The X-ray measurement of the density is doubtless more accurate than Bridgman's estimate.

Diffracted intensities measured from peak areas are compared in Table 1 with theoretical intensities for the structure of Figure 2, calculated from the expression

$$I = C\frac{1 + \cos^2 2\theta}{\sin^2\theta \, \cos\theta} \, f^2(\theta)e^{-2B\sin^2\theta/\lambda^2},$$

where θ is the Bragg angle, $f(\theta)$ the scattering factor for oxygen,[12] and C is a scaling factor chosen to make $I(110) = 100$. The temperature parameter B is unknown, but a value 0.7 A^2 can be calculated by the theory of Debye[13] from the value[3] $B = 2.4$ A^2 for ice I at $-50\,°$C. The needed Debye temperature of ice VII can be obtained from that of ice I[14] on the basis[15] of proportionality to $\beta^{-1/2}\,\rho^{-1/6}$, where ρ is the density and β the compressibility.[1, 16] The rather good agreement between calculated and observed intensities in Table 1 supports the structural interpretation given. It appears that the measured intensities for ice VII are not greatly affected by geometrical factors in the high-pressure instrument, over the range of Bragg angles involved.

Bertie, Calvert, and Whalley[17] have recently reported X-ray powder data for ice VI and VII, obtained at atmospheric pressure from samples quenched in liquid nitrogen. Their data for ice VI agree well in general with ours (Table 2), our spacings being smaller because of the confining pressure. For ice VII, however, these authors find many more lines than we do. Their three strongest lines can be indexed on the basis of a body-centered cubic cell having $a = 3.41$ A, and can thus be matched with the corresponding lines of our pattern, though the relative intensities disagree (Table 2). None of the additional lines reported can be recognized in our patterns (with the possible exception of a low peak at 29.9°, identified as Q in Fig. 3). Although our high-pressure diffractometer measurements cannot detect lines as weak as is possible by the photographic methods used to obtain the quenched patterns, it is evident by comparison that the additonal lines, if present at all, are considerably weaker relative to the lines of the body-centered-cubic structure in the high-pressure patterns than they are in the quenched low-pressure pattern reported.

Discussion.—Our results show that ices II, V, and VI have essentially the same structure when quenched in liquid nitrogen and released to atmospheric pressure as they do under pressure, within their fields of stability. This does not appear to hold for ice VII.

Under pressure, ice VII has the body-centered cubic structure shown in Figure 2. Each water molecule is surrounded by 8 nearest neighbors. One can assume that it is hydrogen-bonded to 4 of these and is in repulsive contact with the other 4, the

TABLE 2

COMPARISON OF X-RAY DATA AT HIGH AND LOW PRESSURE*

Ice VI				Ice VII			
P = 8 kbar (T = −50°C)		P = 0 (T = −190°C)		P = 25 kbar (T = −50°C)		P = 0 (T = −190°C)	
d	I	d	I	d	I	d	I
—	—	4.3	8			4.0	2
—	—	3.6	8			3.5	<1
—	—	3.4	5			3.22	<1
3.09	10	3.12	13	2.34	100	2.42	100
2.87	5	2.91	8			2.27	2
2.71	60	2.75	90			2.09	3
2.59	40	2.63	50			1.91	1
2.49	100	2.51	100			1.75	2
2.39	5	2.43	8	1.64_5	32	1.70	6
2.18	15	2.21	25			1.57	1
2.05	10	2.10	13			1.42	3
Masked (Be)		2.01	20	1.35	9	1.39	9
1.94	15	1.97	20			1.37	<1
1.81	5	1.85	17			1.22	2
1.77	3	1.75	1	1.16	4	1.20	1
1.62	10	1.64	25			1.11	1
1.54	10	1.56	20	1.04	6	1.08	2
1.46	20	1.48	25	0.95	2	0.99	<1
1.44	2	1.44	3	0.88	1.5		
1.39	5	1.41	12				

* *d*-spacings in A. Low-pressure data by Bertie, Calvert, and Whalley.[17]

hydrogen bonds being tetrahedrally arranged. One can also assume[4] that the proton positions are disordered, in the same sense as they are in ice I or ice Ic ("cubic ice").[3, 7, 18] The structure is therefore described statistically as follows: space group $Pn3m(O_h^4)$, $a = 3.30$ A, O in 2 (*a*) (000, $^1/_2$ $^1/_2$ $^1/_2$), $^1/_2$ H in 8(*e*) (*xxx*, etc.), with $x \cong 0.17$. The additional reflections permitted by the hydrogen atom arrangement but not by the oxygen arrangement can be expected to be too weak to observe by the methods used here.

The ice VII structure consists of two interpenetrating but not interconnecting frameworks of ice Ic-type. Topologically it is identical to the structure of cuprite, Cu_2O, and the oxygen atoms have the same arrangement in the two structures.[19] The density of ice VII (1.66) would be exactly twice that of ordinary ice (0.92), except for the fact that the hydrogen bond length is 2.86 A in ice VII (at 25 kbar pressure), as compared to 2.76 A in ice I and Ic (at atmospheric pressure). The increase is caused by the four repulsive contacts, which have the same O—O distance as the four bonds. An O—O contact distance of about 2.80 A is usual in oxygen coordination polyhedra about cations,[20] and in ice II there is evidence that oxygen-oxygen repulsion at a distance of about 3.3 A becomes large enough to cause appreciable distortion of hydrogen bond lengths.[4]

There is no obvious reason why the ice VII structure should not be quenchable at low enough temperature, so that it could be held metastably at atmospheric pressure. The same would not hold for the hypothetical cubic-closest-packed structure of Figure 1, which on release of pressure could always distort (in a martensitic-type transformation) so as to decrease its internal energy. If, upon quenching, the water molecules in ice VII became ordered in a scheme like that in Figure 1, the hydrogen bond energy could probably be increased a little by distortion to a body-centered tetragonal structure ($c/a = 1.10$). However, the X-ray pattern of the quenched phase in this case would simply involve splitting of the powder lines of the high-pressure phase, unlike the quenched pattern reported.[17] From

the high-pressure data, a cubic cell size $a = 3.41$ A is predicted at atmospheric pressure (see below), in agreement with the pseudocell that accounts for the strongest lines of the quenched pattern. Quenched ice VII appears to involve a superstructure, which might be due to electrostatic interaction between the independent ice Ic frameworks, or to a different scheme of proton ordering than the one contemplated above. Such a superstructure is not detectable in our measurements on ice VII under pressure.

Crystal-energy methods can readily be applied to the ice VII structure, and allow evaluation of the repulsive interaction between nonhydrogen-bonded water molecules, a quantity not hitherto available. The details will be reported elsewhere. They make possible a prediction of the lattice constant at atmospheric pressure, as mentioned above, and they make it possible to predict the relative stability of the ice VII structure and the hypothetical cubic-closest packed structure (Fig. 1) for high-pressure ice. It is found that at pressures as high as 220 kbar, the free energy of the hypothetical close-packed structure remains more than 2 kcal mole^{-1} greater than that of ice VII; there is no indication that the hypothetical structure would be stabilized at higher pressures. Hence, ice VII appears truly to be the "ultimate" high-pressure ice phase, in the sense that it will remain stable up to a pressure so high as to effect large changes in the internal bonding of the water molecule, yielding thereby a substance with physical properties very different from those associated with ice in its known forms.[21] At some intermediate pressure, the hydrogen bonds in ice VII should become symmetrical. This pressure lies well above 220 kbar, since the predicted hydrogen bond length at 220 kbar is 2.57 A. whereas a symmetrical bond would involve a bond length[22] of about 2.35 A. We cannot predict whether the transition to the symmetrically bonded structure would be gradual or would appear as a phase change with abrupt decrease in volume.

Summary.—From high-pressure X-ray measurements, the structure of ice VII is found to involve a body-centered-cubic arrangement of water molecules, and consists of two interpenetrating but not interconnecting hydrogen-bonded frameworks of the type present in ice Ic (low-pressure "cubic ice"). This structure represents the densest form of H_2O that can be produced without making drastic changes in the internal bonding of the water molecule, and that therefore will have icelike physical properties in common with the lower-pressure forms of ice.

[1] Bridgman, P. W., *Proc. Am. Acad.*, **47**, 441 (1912); *J. Chem. Phys.*, **3**, 597 (1935); *ibid.*, **5**, 964 (1937).

[2] Pistorius, C. W. F. T., M. C. Pistorius, J. P. Blakey, and L. J. Admiraal, *J. Chem. Phys.*, **38**, 600 (1963).

[3] Peterson, S. W., and H. A. Levy, *Acta Cryst.*, **10**, 70 (1957); Londsdale, K., *Proc. Roy. Soc.* (*London*), **A247**, 424 (1958).

[4] Kamb, B., *Acta Cryst.*, in press; Kamb, B., and S. K. Datta, *Nature*, **187**, 140 (1960).

[5] Pauling, L., *The Nature of the Chemical Bond* (Ithaca: Cornell Univ. Press, 1960), p. 404; Kasper, J. S., and K. Londsdale (ed.), *International Tables for X-ray Crystallography* (London: Kynoch Press, 1959), vol. 2, p. 343.

[6] Darling, B. T., and D. M. Dennison, *Phys. Rev.*, **57**, 218 (1940).

[7] Pauling, L., *J. Am. Chem. Soc.*, **57**, 2680 (1935).

[8] Davis, B. L., and L. H. Adams, *J. Phys. Chem. Solids*, **25**, 379 (1964).

[9] Kennedy, G. C., and P. N. LaMori, *J. Geophys. Res.*, **67**, 851 (1962).

[10] Bertie, J. E., L. D. Calvert, and E. Whalley, *J. Chem. Phys.*, **38**, 840 (1963).

[11] Adams, L. H., *J. Wash. Acad. Sci.*, **11**, 45 (1921).

[12] Hoerni, J. A., and J. A. Ibers, *Acta Cryst.*, **7**, 744 (1954).

[13] Kasper, J. S., and K. Londsdale (ed.), *International Tables for X-ray Crystallography* (London: Kynoch Press, 1959), vol. 2, p. 241.

[14] Owston, P. G., *Advan. Phys.*, **7**, 171 (1958).

[15] Kittel, C., *Solid State Physics* (New York: John Wiley and Sons, Inc., 1956), p. 129.

[16] Bass, R., D. Rossberg, and G. Ziegler, *Z. Physik*, **149**, 199 (1957).

[17] Bertie, J. E., L. D. Calvert, and E. Whalley, *Can. J. Chem.*, **42**, 1373 (1964).

[18] Blackman, M., and N. D. Lisgarten, *Advan. Phys.*, **7**, 189 (1958).

[19] Bragg, W. L., *Atomic Structure of Minerals* (Ithaca: Cornell Univ. Press, 1937), p. 90.

[20] Pauling, L., *The Nature of the Chemical Bond* (Ithaca: Cornell Univ. Press, 1960), p. 542.

[21] Gränicher, H., *Phys. Kondens. Materie*, **1**, 1 (1963); Bertie, J. E., and E. Whalley, *J. Chem. Phys.*, **40**, 1646 (1964).

[22] Ref. 20, p. 484.

STUDIES ON THE BIOSYNTHESIS OF CHLOROPHYLL: CHEMICAL INCORPORATION OF MAGNESIUM INTO PORPHYRINS*

BY STUART J. BAUM,† BRUCE F. BURNHAM, AND ROBERT A. PLANE

DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY

The incorporation of magnesium into porphyrin is a key step in the biosynthesis of chlorophyll. Previous investigators of this reaction have always found it necessary to employ an activated form of magnesium (e.g., magnesium alkoxides,[1] Grignard reagent,[2] or magnesium violigen[3]) and strictly anhydrous conditions. This report concerns the first chemical preparations of magnesium porphyrins under nonanhydrous conditions.

We have found that magnesium is incorporated into the porphyrin nucleus when certain magnesium salts and the tetrapyrrole are heated to reflux in either pyridine or in *n*-propanol. The addition of a small quantity of water (2%) to pyridine or propanol has little or no effect upon either the reaction products or the reaction time, whereas larger amounts of water, while not affecting the over-all outcome of the reaction, do markedly retard the reaction. Furthermore, the addition of a number of other solvents to the reaction mixtures does not influence either the reaction products or the reaction time.

In a preliminary study of the reaction, pyridine was added, without predrying, to a flask containing deuteroporphyrin dimethyl ester[4] and magnesium perchlorate. The reaction mixture was heated to reflux and, at intervals, aliquots were removed and analyzed with a recording spectrophotometer. The reaction was essentially complete after 6 hr. In later studies, the reaction mixtures were sealed in glass ampules and the reaction was carried out in the autoclave at 18 lb pressure for 2 hr. The reaction was complete in this time. If the ampules are placed in a water bath at 70°C, the reaction is 50 per cent complete in 10 hr.